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16. ABSTRACT

The photochemical treatment of hazardous waste can be optimized by taking into account various factors that influence the rates of photochemical reactions. Physical factors that facilitate photochemical treatment include: (1) maximizing the irradiated surface to volume ratio of the system, (2) selecting a light source with a spectrum that strongly overlaps the absorption spectrum of the chromophore, and (3) vigorously mixing the reaction mixture. Although hazardous wastes are degraded by direct absorption of light, the overall rate of light-induced reactions can usually be accelerated by adding to the treatment system various dissolved or particulate substances that, on light absorption, produce reactive excited states or free radicial intermediates that react with the waste. Examples of such additives include ozone, peroxides, semiconducting metal oxides such as titanium dioxide, and various organic photosensitizers that efficiently photoproduce excited triplet states.

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JOURNAL ARTICLE

Factors affecting the photochemical treatment of hazardous waste

By Richard G. Zepp

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Treatment of wastes by photochemical reaction differs from usual chemical techniques in that the prime reactant, light, somehow must be added to the system, which is usually contained in a glass vessel or outdoor treatment system. The light source may be the sun or a lamp of some type.

Photochemical treatment can be optimized by taking into account various factors that influence photoreaction rates. The rate of a photoreaction is proportional to the light absorption rate by the chromophore, $I_a(\lambda)$, and to the overall quantum yield, ϕ. The overall quantum yield is the fraction of absorbed light at a wavelength that results in the photoreaction of some substrate. Both the light absorption rate and the overall quantum yield are dependent on wavelength, although the wavelength dependence of the quantum yield for direct photolysis of organic compounds usually is small in solution.

The light absorption rate for a given treatment system can be optimized in several ways. First, and most important, the light source and material of the reaction cell through which the light passes should be selected to maximize the overlap of the electronic absorption spectrum of the chromophore and the spectrum of the light that enters the reaction medium. Finlayson-Pitts and Pitts (*1*) and Zepp (*2*) discuss various lamps that are commonly used. Second, retardation by light attenuation effects can be minimized by maximizing the surface area to volume ratio for the photoreactor. Third, especially in systems where all the incident light is absorbed, it is especially important that the reaction mixture be well mixed to avoid transport limitations on the conversion rate.

Two general types of photoreactions can be used in photochemical treatment. Direct photolysis involves light absorption by the substrate followed by chemical reaction of the substrate in its electronically excited state. Direct photolysis is the only pathway for photoreaction in a reaction medium that is transparent to the incident light. Indirect photoreactions involve chemical reaction of a substrate that is induced through light absorption by another substance in the system. Indirect photoreactions are mediated by excited states of photosensitizers, by free radicals of various types, and by other short-lived reactive transients.

In principle, direct and indirect photoreactions may occur in parallel in a treatment system. General approaches have been developed to compute light-induced reaction rates as a function of system composition, spectral irradiance of the light source, and quantum yield (*2–4*). Applications of direct photoreaction and of several types of indirect photoreactions to hazardous-waste treatment are discussed in the balance of this view.

This view is based on the extended abstract of Richard Zepp's paper presented at the Fall ACS meeting, held in New Orleans on August 30–September 4, 1987. This paper was the first submitted to *ES&T* on the bulletin board for rapid publication. As part of our effort to reduce the time to publication, *ES&T* encourages authors to submit timely articles via our bulletin board.

Direct photoreactions

A wide variety of reactions occur on direct absorption of light by hazardous wastes. For general background on this subject, the book by Turro (*5*) is particularly useful for organic photoreactions; books by Balzani and Carassiti (*6*) and by Adamson and Fleischauer (*7*) provide an overview of inorganic photoreactions. Xenobiotic by-products are more specifically described by Crosby and co-workers (*8*) and Sundstrom and Ruzo (*9*) among many others. Photoreactions of xenobiotics can lead to mineralization. Moreover, the products of direct photoreactions of biologically refractory xenobiotics are sometimes considerably more susceptible to biodegradation than the xenobiotic itself (*10*).

Generally the overall quantum yields, reaction products, and, to a

lesser extent, the electronic absorption spectra are very sensitive to the nature of the reaction medium. For example, photoreactions of organic xenobiotics in micelles formed by surfactants have been shown to proceed with much different rates and products than observed in water (*11*). Furthermore, direct photoreactions of ionizable compounds such as chlorophenols are often very sensitive to pH (*10*). As a final example, the presence of electron donors such as amines can greatly enhance the overall quantum yields of certain chlorinated aromatic compounds such as hexachlorobenzene (*12*).

Photosensitized reactions

Photosensitized reactions involve the transfer of electronic energy from an excited sensitizer either directly to the substrate or to dioxygen. Energy transfer to molecular oxygen results in formation of singlet oxygen, an excited form of dioxygen that can rapidly oxidize some types of xenobiotics. Certain dyes are particularly effective photosensitizers in treatment systems. Dye photosensitizers have very high light absorption rates with sunlight and with most lamps. They also cross intersystem to long-lived triplet states that efficiently participate in energy-transfer reactions. Some of the recent research on this promising treatment technique has been discussed by Eisenberg and co-workers (*13*).

UV–ozone oxidations

The combination of ultraviolet light (< 300 nm) and ozone has proved to be a particularly effective technique for the oxidation of pollutants. The photolysis of ozone in water leads to production of hydrogen peroxide, which then reacts with ozone to form a potent oxidant, the hydroxyl radical (*14, 15*). Hydroxyl radicals react rapidly with most xenobiotics by abstracting hydrogen atoms or by adding to aromatic systems and double bonds. This treatment procedure has been recently reviewed by Peyton and Glaze (*15*).

Semiconductor reactions

Irradiated semiconductors are versatile reagents that show promise for treatment of hazardous wastes. Titanium dioxide has been shown to effectively photocatalyze the reductions of chlorinated organics and the oxidation of various other organic chemicals (*16-19*). Other metal oxides potentially could be used in the photochemical treatment of hazardous wastes.

This discussion is by no means meant to be comprehensive, but rather to provide some indication of the potential of photochemical reactions for treatment of hazardous wastes. Any substance that efficiently photolyzes to produce reactive free radicals may be useful in photochemical treatment systems. Readily available reagents such as nitrate (*20*) and humic substances (*4, 21*) photoreact to form free radicals and thus possibly could be used in such treatment processes.

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